Supplementary Information (SI) for ChemComm.

Supporting Information

Manuscript ID:

Title: Electrochemical Na doping to spent lithium-ion batteries takes on an entirely new look

Xiang Li[1,#], *Zeyuan Bu*[1,#], *Haining Liu*[1], *Lihao Qin*[1], *Binghao Qiu*[1], *Ke Sun*[1], *Zengshi Zhang*[1], *Shuxuan Liao*[1], *Leqing Zhang*[1], *Xiaoshan Wang*[1], *and Qiang Li*[1,*]

[1] College of Physics, Weihai Innovation Research Institute, College of Materials Science and Engineering, Qingdao University, Qingdao 266071, China

# These authors contributed to this work equally.

* Corresponding author E-mail address: liqiang@qdu.edu.cn (Q. Li).

The Supporting information include:

Section S1. Experimental section

Synthesis of Recycle-$LiMn_2O_4$

The spent $LiMn_2O_4$ batteries were discharged to nearly 0 V, disassembled into different parts, and the active material as well as the conductive agent and the binder on the aluminum foil were scraped manually. The scraped powder was used as a precursor for the preparation of the precursor of Recycle-$LiMn_2O_4$. The obtained precursor was calcined for 20 h at 800°C in air to remove the binder and conductive additive from it, and Recycle-$LiMn_2O_4$ was obtained after sintering was completed.

Materials characterizations

The crystal phase of the samples were detected using an X-ray diffraction (Smart Lab 3 kW) with a Cu Kα radiation source over a 2θ range of 10° to 80°. Transmission electron microscopy (TEM, JEM-2100F) and Ultra-high Resolution Emission Scanning Electron Microscope (SEM, HITACHI-SU8010) were used to analyze the morphology and structure of the samples. The battery for the magnetic measurement is unpacked at room temperature in a glove box filled with argon gas to exclude influences other than the electrodes themselves. Magnetic measurements were performed on a physical property measurement system (PPMS, Quantum Design). Magnetic susceptibility as a function of temperature (MT) curve magnetic measurements on the electrode materials were carried out, the electrodes were washed in the glovebox after being discharged to specific potential, and 0.1 T magnetic field was selected for MT at 10-300 K, and fitting the magnetic moments used to determine the Mn valence state. Electron Paramagnetic Resonance (EPR) spectra were collected on EMXplus-6/1/P/L EPR spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo Scientific ESCALAB 250XI photoelectron spectrometer. The internal valence state of the sample at different potentials was confirmed. Inductively coupled plasma (ICP) testing was conducted on the iCAP™ PRO ICP-OES system.

Electrochemical Measurements

The positive electrode was made from a slurry mixture of recycled material powder (80%), super pll (10%), polyvinylidene (PVDF) (10%) and N-methyl-2-pyrrolidone (NMP). Sodium flakes and glass cellulose membrane (Whatman GF/D) were used as anode and diaphragm, respectively. The electrolyte was used 1 mol L^{-1} $NaClO_4$ dissolved into a mixture of anhydrous ethylene carbonate (EC, GR, Aladdin) and diethyl carbonate (DEC, GR, Aladdin) (1:1 by volume) with 5% FEC (NC-008) was acted as the electrolyte. Battery components were assembled as button cells in an argon-filled glove box (both H_2O and O_2 are lower than 0.1 ppm). Cyclic voltammetry (CV) was performed at various scanning rates between 1.5 and 4.2 V (versus Na^+/Na) on a CHI660E electrochemical workstation. On Land battery test system (Land, CT2001A), galvanostatic charge and discharge tests are performed with different current densities in the cut-off voltage range of 1.5~4.2 V. Cycling data were collected at room temperature by a battery blue electrical measurement system. The rate is 50 mA g^{-1}.

Section S2. Supplementary equations

Equation S1. The classical formula established by Weppner and Huggins

$$D_{app}=\frac{4}{\pi\tau}(\frac{m_B V_M}{M_B S})^2(\frac{\Delta E_S}{\Delta E_\tau})^2$$

Eq. S1 Using the galvanostatic intermittent titration technique (GITT), a pulse (τ) lasting 20 minutes is followed by a relaxation period of 1 hour. All required parameters can be obtained from known conditions, where τ represents the time duration of the excitation current, m_B denotes the active mass, V_M is the molar volume of the electrode, M_B is the molar mass of the electrode, S signifies the electrode area, ΔE_S indicates the change in steady-state voltage, and ΔE_τ refers to the change in transient voltage.

Equation S2. Curie-Weiss equation

$$\chi = \frac{C}{T - \theta_{CW}}$$

Section S3. Supplementary Figures

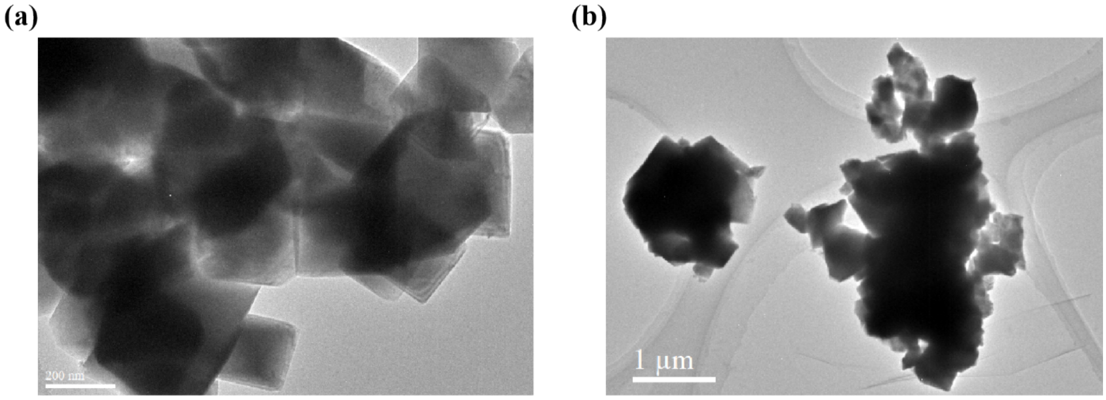

Fig. S1 (a, b) HRTEM images of the sintered recycled material.

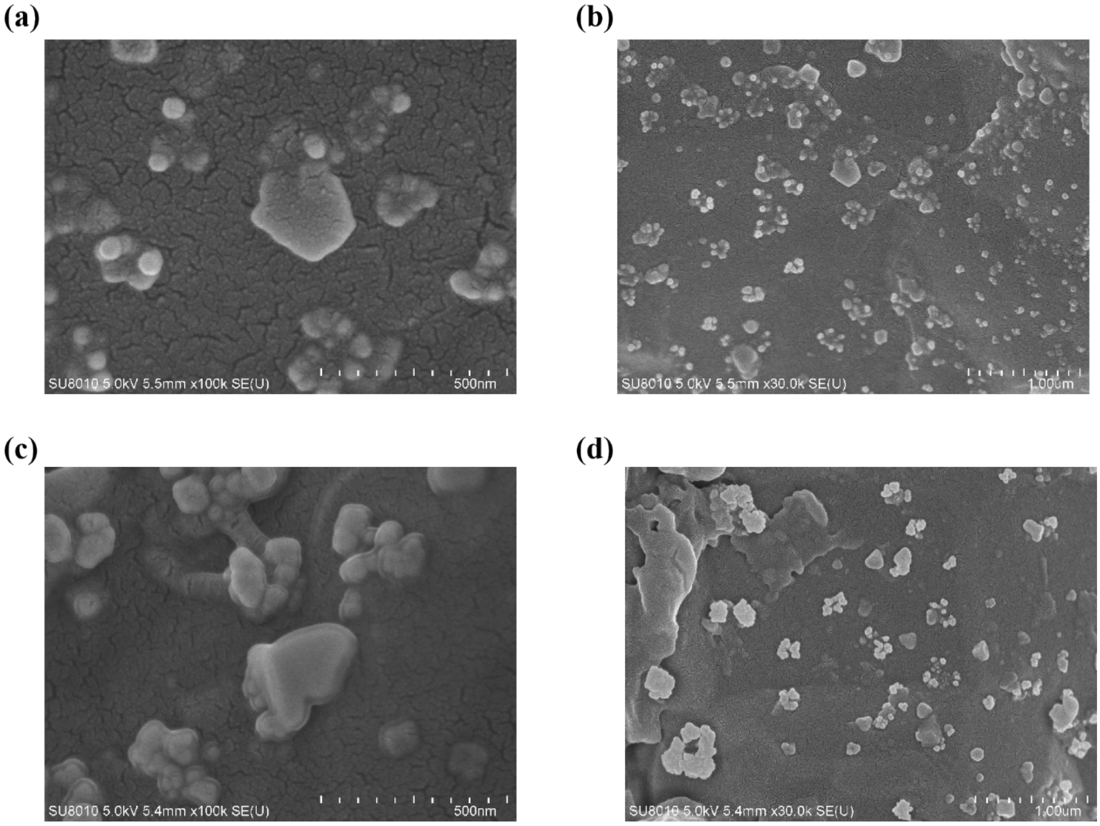

Fig. S2 (a, b) SEM images of the recycled materials before. (c, d) SEM images of the recycled materials after sintering.

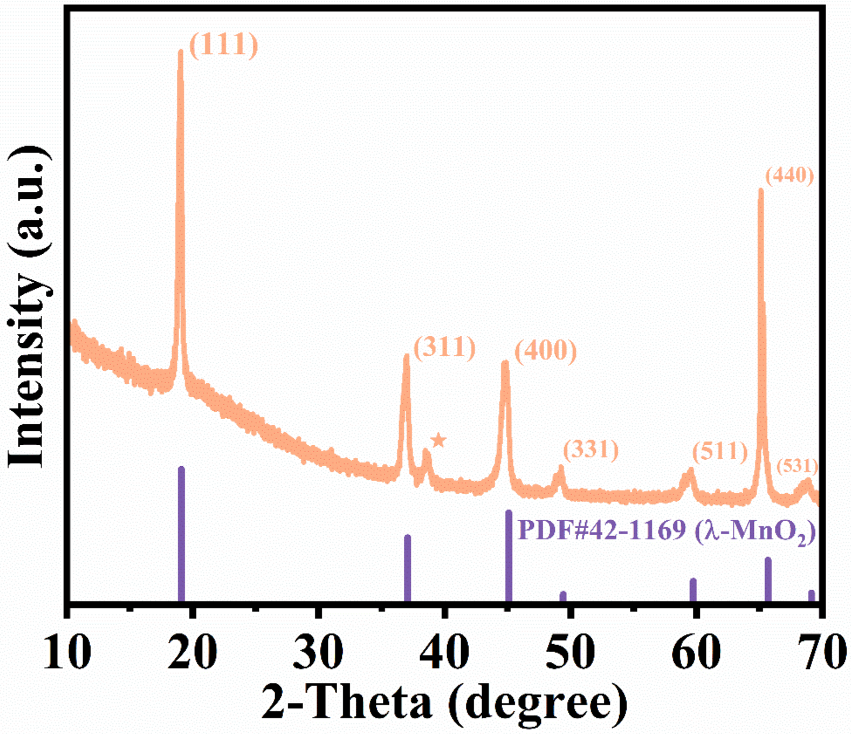

Fig. S3 XRD pattern of D-LMO.

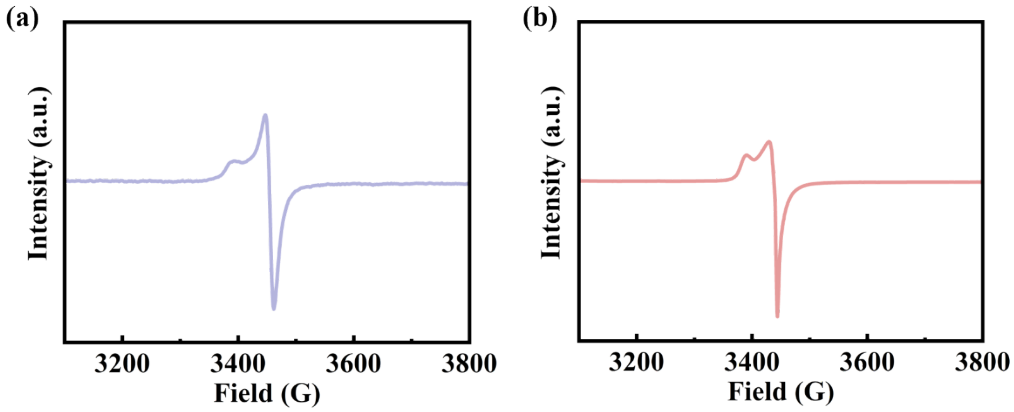

Fig. S4 (a, b) EPR spectra of carbon electrode and lithium intercalation in carbon electrode.

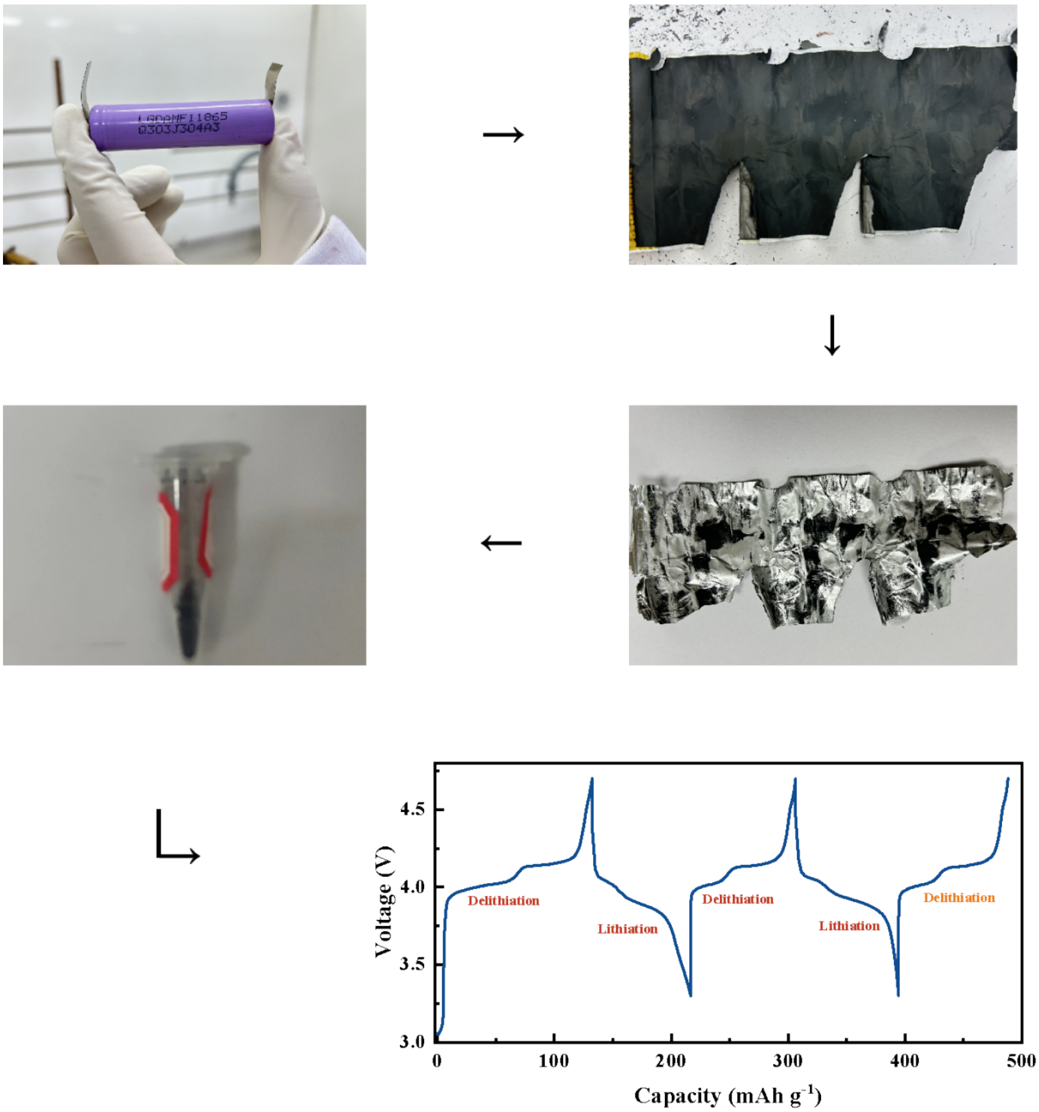

Fig. S5 Schematic diagram of the recycling process.

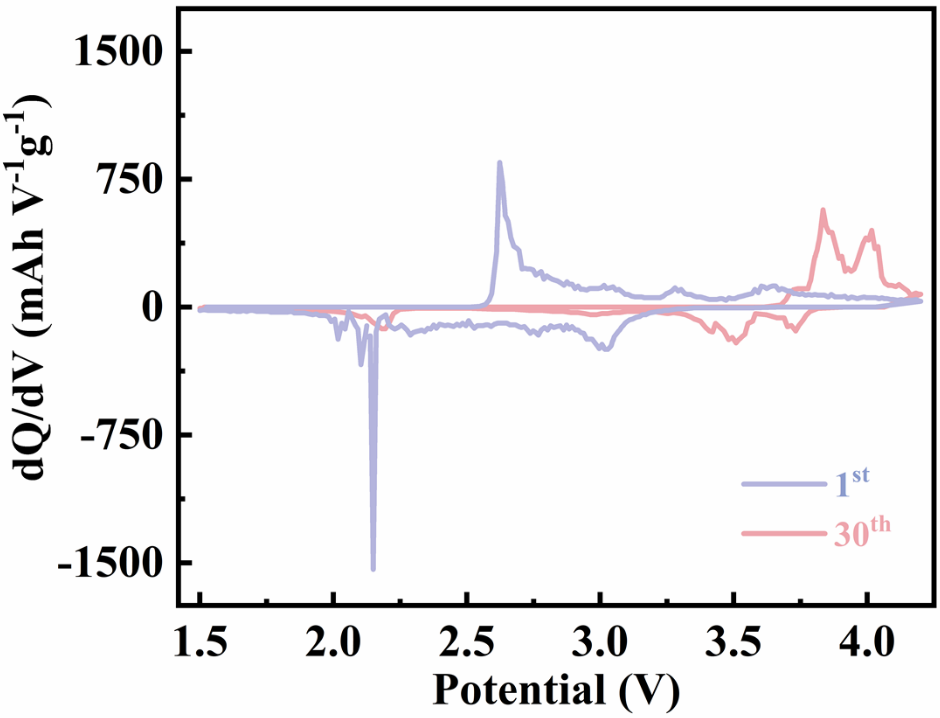

Fig. S6 Differential dQ/dV plots of D-LMO electrode before and after 30 cycles.

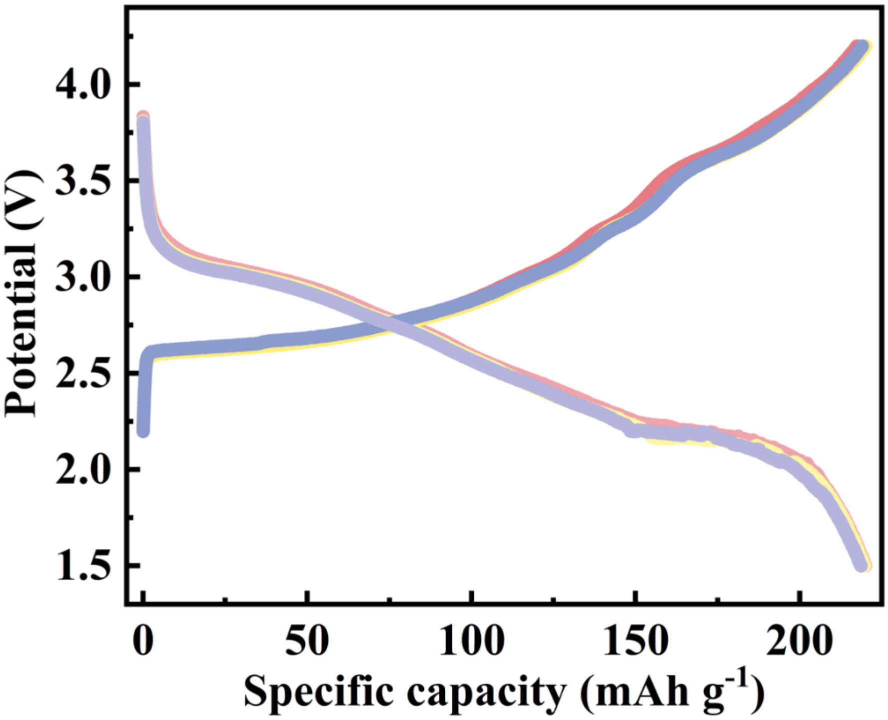

Fig. S7 Electrochemical curves of charge/discharge cycles for the 31st, 33rd, and 35th cycles.

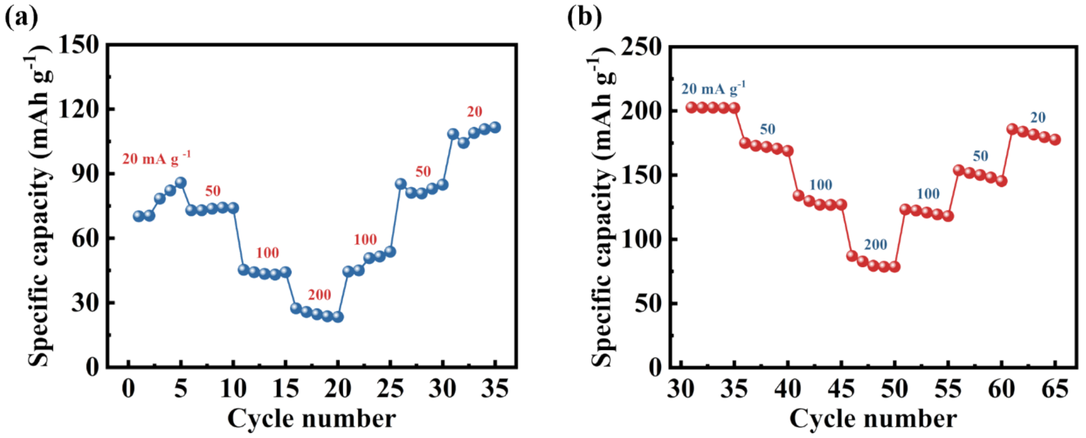

Fig. S8 (a, b) Rate performance for D-LMO electrode in sodium cells and after 30 cycles at 50 mA g^{-1} in sodium cells.

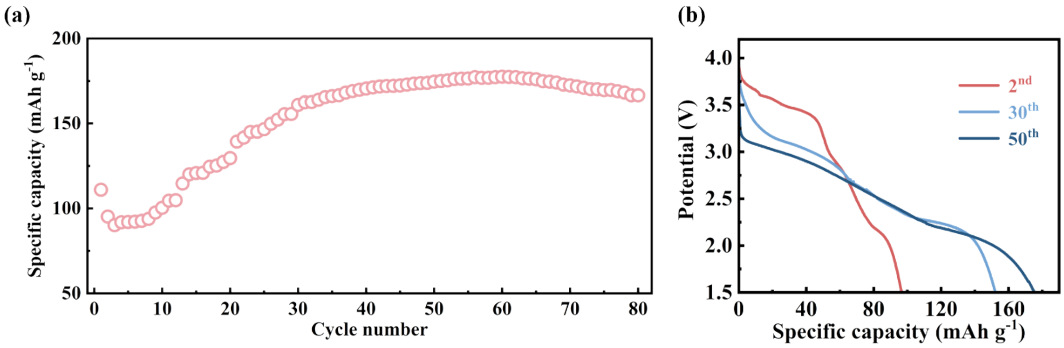

Fig. S9 Characterization test results of Recycled $LiMn_2O_4$: (a) cycle performance in sodium cells as cathode materials. (b) Electrochemical discharge curves of cycles for the 2nd, 30th, and 50th cycles.

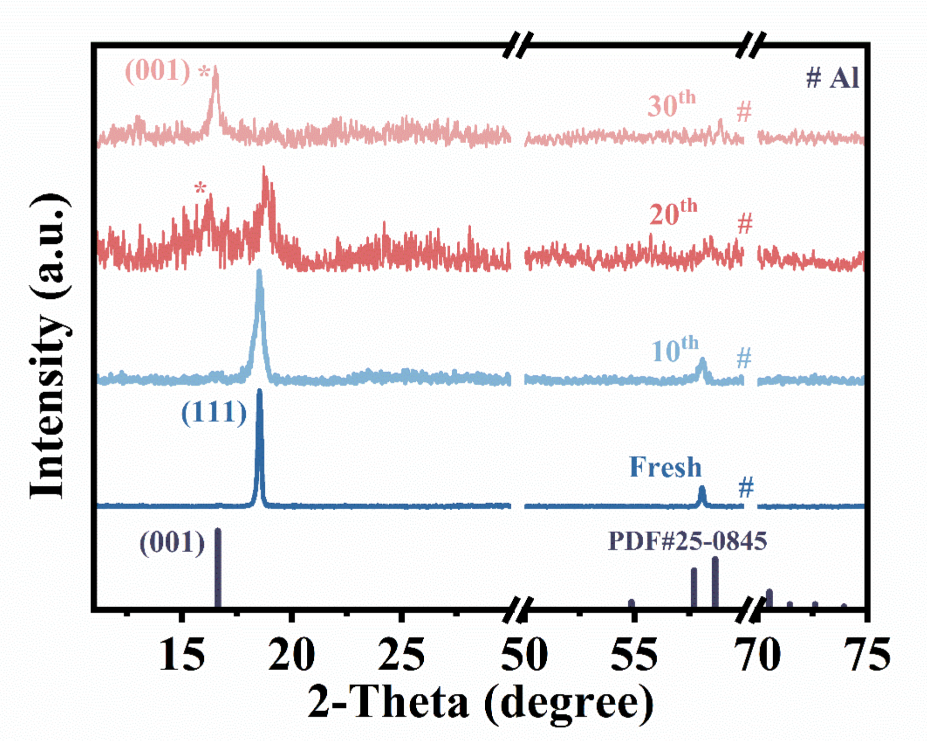

Fig. S10 XRD pattern of D-LMO with different charge-discharge cycles.

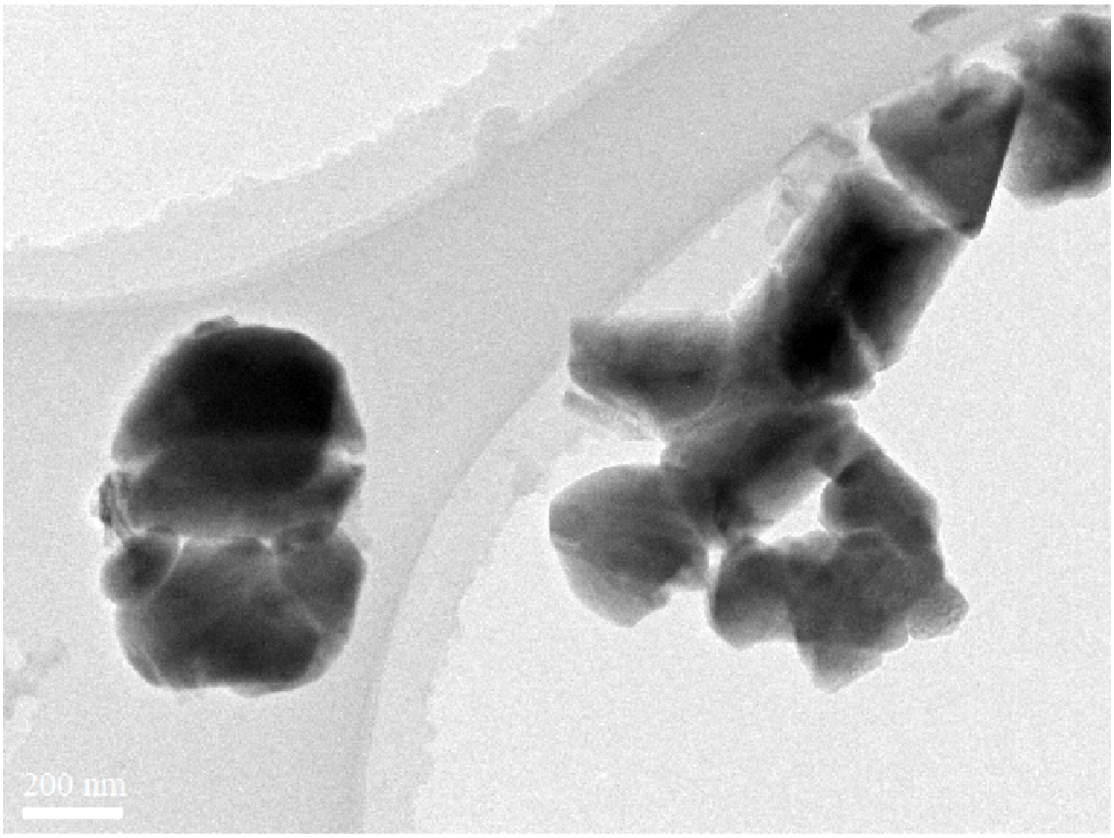

Fig. S11 HRTEM image of charge/discharge cycles after 30 cycles.

Section S4. Supplementary Tables

Table S1		Li %	Mn %
Before	Molar ratio	6.05	14.7
After sintering		5.90	20.3

Table S1. ICP-OES test results: Table of Li and Mn element contents in spent $LiMn_2O_4$ before and after sintering.

Table R2		Li %	Mn %
D-LMO	Molar ratio	0.42	35

Table S2. ICP-OES test results: Table of Li and Mn element contents in D-LMO.